

Structural Changes of Bimetallic Pd_x/Cu_(1-x) Nanocatalysts Developed for Nitrate Reduction of Drinking Water

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ABSTRACT

Reductive removal by hydrogenation using supported Pd/M (M= Cu, Pt, Ag, Co, Fe, Mo, Ni, Rh, Ir, Mn and Cr) bimetallic catalysts has emerged as a promising alternative for nitrate removal in drinking water [1]. Fundamental understanding how the atomic arrangement of Pd and a second element, such as Cu, affect the activity nitrite reduction and selectivity of dinitrogen will be accomplished by coordinated synthesis (Shapley), activity/selectivity/efficiency measurements (Werth) and nanostructure determination (Yang & Xu). In this paper, we report a systematic study of novel polyvinylpyrrolidone (PVP) stabilized nanoscale Pd-Cu colloids, with homogeneous and narrow size distribution, with Pd: Cu ratios varying from 50:50 to 90:10. Initial measurements on catalytic activity for nitrate reduction demonstrated a dependence on the relative composition. Electron microscopy studies, including Z-contrast imaging [2], energy-dispersive X-ray emission (EDX), electron diffraction and high-resolution electron microscopy (HREM), revealed a surprising change in structure at the 80:20 Pd-Cu composition, where, with less than 80% Pd, the nanoparticle forms a core-shell structure but for nanoparticles containing 80% or more Pd, it is homogeneous. We are at the pivotal point of directly correlating these nano-structures with the catalytic activity. Such an understanding is essential for the efficient development of catalysts for the purification of drinking water.

INTRODUCTION

Presently nitrate in drinking water is either not removed, or it is removed using ion exchange resins. The former presents health risks [3]; the latter is expensive because waste streams must still be treated when the resins are regenerated [4]. Nitrate is a stable and highly soluble ion with a low potential for co-precipitation or adsorption, so that removal of nitrates using conventional water treatment is difficult. An exciting and recently emerging approach involves hydrogenation of oxidized contaminants using supported bimetallic metal catalysts, such as Pd-Cu bimetallic catalysts [5-10]. However, these promising catalysts exhibit inadequate

selectively toward nitrogen production, such as formation of the side product, ammonia, which is undesirable in drinking water. Further optimization of the current treatment technologies and developing emerging technologies for nitrate removal from both public and (especially) domestic water supplies is needed. Therefore, we expect a significant saving to result when nitrate can be removed from drinking water sources using bimetallic catalysts. Results from this project are expected to identify the most promising catalysts to use for the reduction of nitrate and other oxidized compounds and to gain fundamental understanding of the reactivity and selectivity of these new catalytic materials.

EXPERIMENTAL DETAILS

Shapley and coworkers have used simultaneous reduction [11-12] in which a mixture of palladium (II) acetate and copper (II) acetate is heated in a primary alcohol in the presence of a stabilizing polymer to synthesize a series of bimetallic Pd/Cu/PVP (PVP=polyvinylpyrrolidone) colloidal nanoparticles, where the Pd:Cu ratio varies from 50:50 to 90:10. Werth will measure the nitrate reduction activity and dinitrogen selectivity of these new catalytic materials, focusing especially on the mass transfer characteristics of a flow system and the influence of co-contaminants typically present in ground and surface waters. Xu & Yang has established the control of particle size in the colloid synthesis approach and 3-dimensional structure of the Shapley's Pd-Cu/PVP colloids by using high spatial-resolution transmission electron microscopy (TEM), high-resolution TEM (HREM), Z-contrast imaging [2], Electron Diffraction and Energy-dispersed Spectroscopy (EDS) techniques [13]. The experiments were performed in a Jeol 2010 FEG TEM and a Philip Tecnai 20 FEG TEM operated at 200Kv. Samples were prepared by suspending the colloids in ethanol under ultrasonic vibration. Some drops of the as-produced suspension were brought onto a holey carbon film on a Ni grid.

RESULTS AND DISCUSSIONS

By altering the synthesis procedure, such as heating temperature and relative concentrations of the precursors as well as the support material, different Pd-Cu nanoparticles could be synthesized, such as a homogeneous Pd-Cu alloy or Pd core surrounded by Cu, which are expected to have different reaction chemistries. Control of particle size in the colloid synthesis approach is evidenced by TEM studies by Xu and Yang on Shapley's Pd-Cu/PVP colloids with composition ranging from 50:50 to 90:10 (see Figure 1). Particle size is distributed in the rather narrow range of 3 to 5 nm. Interestingly, the average particle size for specific compositions changes from near 5 nm for the 90:10 colloids to near 3 nm for the 50:50 colloid (see Figure 2).

This synthesis method clearly allows for tighter control of both the size and the stoichiometry of bimetallic particles than the "classical" method of support impregnation with the separate metal salts followed by calcinations and reduction. The various nanoparticles were characterized with Z-contrast imaging as well as by energy dispersive X-ray spectroscopy (EDS) on a dedicated scanning transmission electron microscope (STEM) and a high-resolution electron microscopy (HREM).

Size distribution-Pd:Cu=60:40

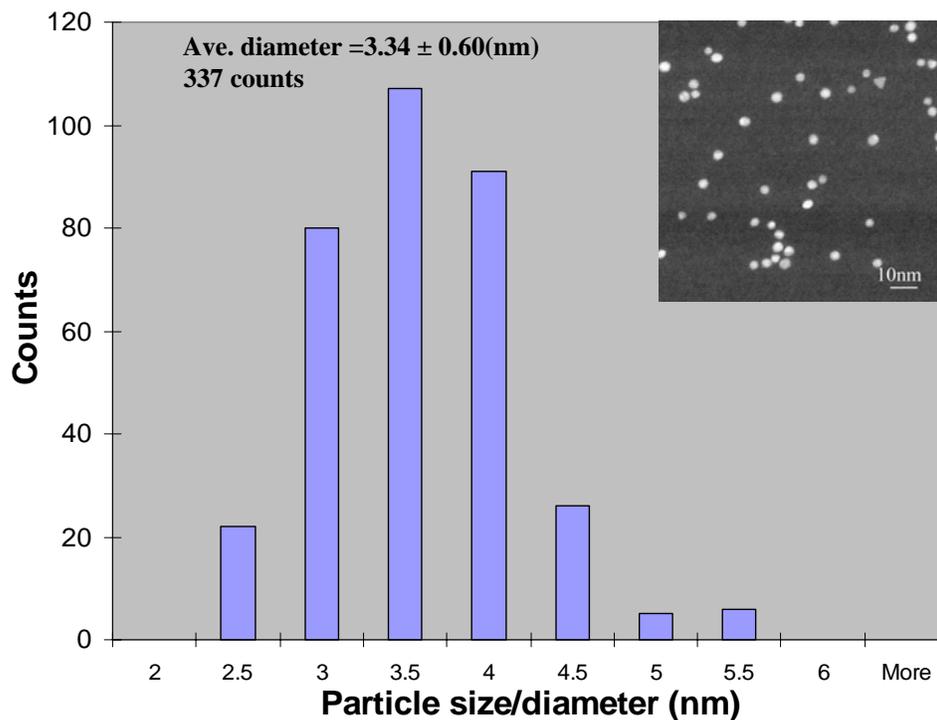


Figure 1. TEM image of Pd-Cu/PVP (PVP=polyvinylpyrrolidone) colloid (Pd:Cu=60:40) and particle size distribution.

Particle size v.s. content of Pd

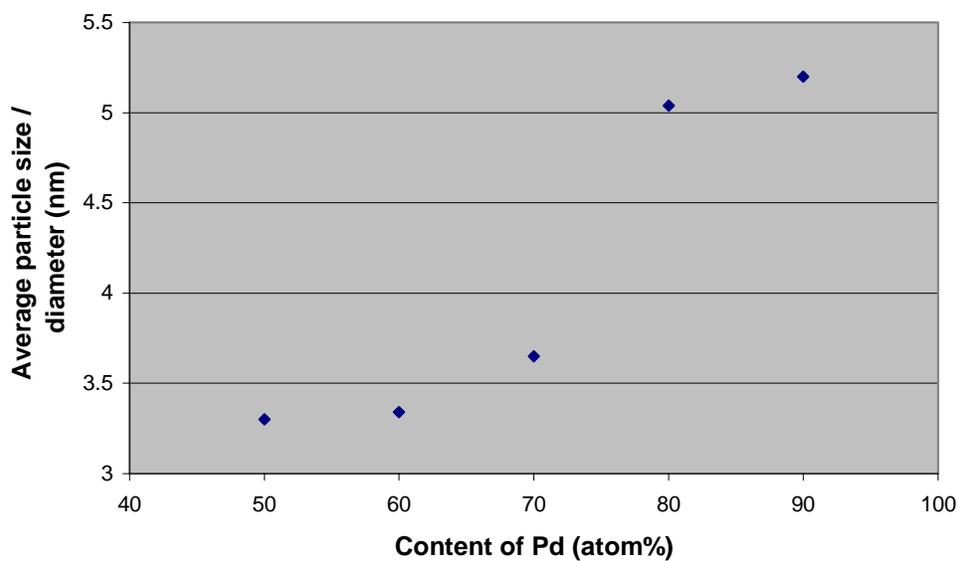


Figure 2. Plot of average particle diameter versus amount of Pd (atomic %). A sudden increase in size is noted between 70 and 80%.

Interestingly, the average particle size for specific composition abruptly changes from near 5nm for the 80:20 (Pd:Cu) colloid to near 3nm for the 70:30 colloid due to a change in structure. HREM images reveal that the particles with 70% or lower amounts of Pd form a core-shell structure with Cu on the outside and Pd on the inside (Figure 3), whereas for the 80 and 90% Pd particles, these are a face-centered cubic (FCC) structure containing a homogeneous mixture of Pd and Cu (Figure 4). These results were also confirmed by EDS elemental maps.

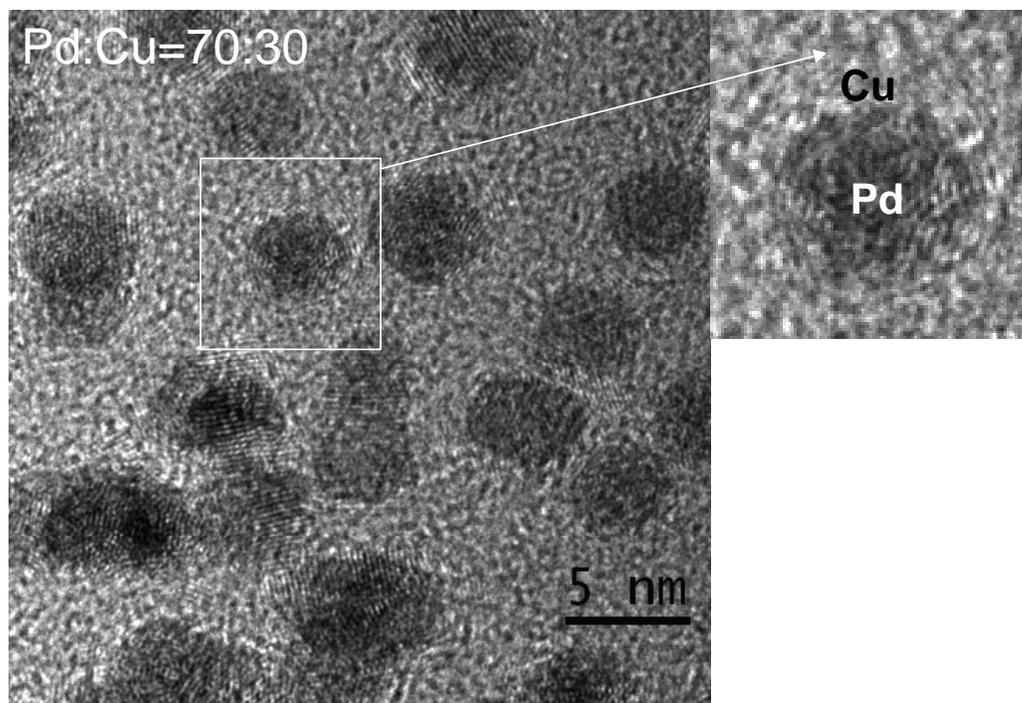


Figure 3. HREM images of the core-shell structure for the 70:30 (Pd:Cu) composition nanoparticles.

We have noted that the nitrate reduction capabilities of the alloy materials depend on the Pd: Cu ratio as 50:50 > 60:40 > 70:30 >>> 80:20, 90:10, where no reduction is seen in the last two cases, at least at room temperature. Further characterization studies are needed to determine whether this is a reflection of the average number of Pd and Cu ensembles on the nanoparticle surface or if it is related to the particle growth mechanisms [14].

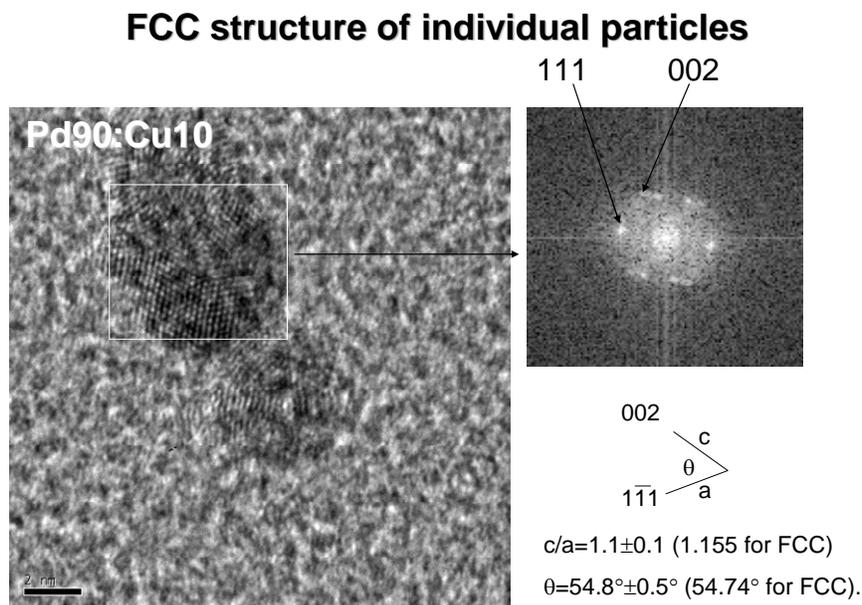


Figure 4. HREM images of the 90:10 (Pd:Cu) homogeneous nanoparticles, and corresponding Fourier transform, which gives a “diffraction” pattern, revealing FCC structure.

CONCLUSIONS

1. Successfully synthesized a range of Pd-Cu bimetallic catalysts with uniform composition and size distributions (3-5nm).
2. Interestingly, the average particle size for specific composition changes from near 5nm for the 90:10 colloids to near 3nm for the 50:50 colloids.
3. A significantly abrupt change of particle size occurs between 70 at% Pd and 80 at% Pd, which is related to the formation of a core-shell structure.
4. The nitrate reduction capabilities of the alloy materials depend on the Pd: Cu ratio as 50:50 > 60:40 > 70:30 >>> 80:20, 90:10, where no reduction is seen in the last two cases, at least at room temperature.

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